



Synthesis and catalytic applications of metal–organic frameworks: a review on recent literature

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Abstract

Metal–organic frameworks (MOFs) are an emerging class of porous materials created by the assembly of inorganic connectors and organic linkers. They have potential applications in fields such as gas storage as well as separation, sensing, catalysis, and drug delivery due to its properties such as flexibility, porosity, high surface area and functionality. Among the various synthetic approaches for the preparation of MOFs, solvothermal and microwave-assisted methods are of particular importance, and hence have been used frequently. They have been recently used as heterogeneous catalysts in Friedel–Crafts reactions, condensations reactions, oxidations, coupling reactions, etc. However, owing to the low thermal stability and moisture sensitivity, their catalytic applications are limited. This short review covers recent developments in the synthetic methods employed for the preparation of MOFs as well as their catalytic applications.

Keywords Metal–organic framework · Synthesis techniques · Stability · Heterogeneous catalyst

Abbreviations

| | |
|------------------------|---|
| H ₂ ,3-pydc | Pyridine-2,3-dicarboxylic acid |
| bpp | 1,3-Bis(4-pyridyl)propane |
| H ₂ bpabdc | 2,5-Bis(phenylamino)-1,4-benzenedicarboxylic acid |
| H ₂ tdc | Thiophene-2,5-dicarboxylic acid |
| H ₄ abtc | 3,3',5,5'-Azobenzene-tetracarboxylic acid |
| ad | Adenine |
| H ₃ btc | 1,3,5-Benzene tricarboxylic acid |
| H ₂ bdc | 1,4-Benzenedicarboxylic acid |
| pdc | 2,6-Pyridinedicarboxylate |
| DMI | 1,3-Dimethyl-2-imidazolidinone |
| DMA | <i>N,N'</i> -Dimethylacetamide |
| DMF | <i>N,N'</i> -Dimethyl formamide |
| THF | Tetrahydrofuran |
| TBHP | <i>tert</i> -Butyl hydroperoxide |
| DMI | 1,3-Dimethyl-2-imidazolidinone |

Introduction

Metal–organic frameworks (MOFs) are a novel class of porous materials recently developed by material scientists. They are crystalline, organic–inorganic hybrid compounds in which metal ions and organic multidentate ligands are linked together by coordinate bonds. MOFs exhibit high surface areas with tunable functionality and pore size, enhanced activity than base metal oxides, shape/size selectivity. As a result, they have been used as hosts for a variety of guest molecules [1–3]. They also find applications in adsorption, catalysis, magnetism, sensing and drug delivery [4–6]. The physical properties of MOFs such as magnetic susceptibility, conductivity and optical characteristics are decided by the nature of metal–organic framework as a solid [7].

Over the last two decades, a lot of research work has been done on MOFs. Transition metals, alkaline earth metals, p-block elements, actinides and even mix metals are used for the synthesis of MOFs. N-containing aromatics or multivalent aromatic carboxylic acids are commonly used organic linkers in MOFs. Based on the size of inorganic building units and ligands as well as framework connectivity, pores and open channels with sizes ranging from angstroms to nanometers can be present [7]. Traditionally used porous materials such as zeolites possess small pore size and silicate materials have too large large. MOFs bridge the gap between these two classes of porous materials. MOFs with

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pore sizes ranging from ultramicropores to mesopores have been reported in literature. However, compared to oxides, MOFs show lower chemical, thermal, and hydrothermal stability [8]. This short review attempts to consolidate the recent developments in the field of MOF synthesis and their catalytic applications.

Synthesis of MOFs

Many methods are available for the synthesis of MOFs. Majority of these occur in liquid phase, where the metal salt and ligand solutions are prepared separately and mixed together or solvent is added to a mixture of solid salt and ligand. Selection of solvent is crucial for the synthesis of MOFs with better characteristics and usually depends on different features like redox potential, reactivity, stability constant, solubility, etc.

Slow evaporation method

In this method, the precursors are dissolved in a solvent or a mixture of solvents. Slow evaporation of the solvent takes place at a particular temperature usually at inert atmosphere. It is a conventional method for the preparation of MOF, without any external energy supply. Solubility of the reagents is a major problem while preparing MOF by this method. Therefore, mixture of solvents can be used to increase the solubility. Though the technique can be employed at room temperature, it is a time-consuming process. Murinzi et al. [9] developed a new supramolecular MOF with cobalt as metal ion and 2, 6-pyridinedicarboxylic acid as linker by slow evaporation method. The synthesized cobalt MOF was found to be effective for detection of L-cysteine. Wang et al. [10] prepared three new metal–organic frameworks, $[\text{Cu}(2,3\text{-pydc})(\text{bpp})] \cdot 2.5\text{H}_2\text{O}$, $[\text{Zn}(2,3\text{-pydc})(\text{bpp})] \cdot 2.5\text{H}_2\text{O}$ and $[\text{Cd}(2,3\text{-pydc})(\text{bpp})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ at room temperature. The latter two complexes showed intense fluorescent emissions in photoluminescent study.

Solvothermal synthesis

Solvothermal method is the most recurrently used method for the preparation of MOFs as it provides a variety of morphologies. In this method, the reaction occurs between the metal salt and the organic ligand in organic solvents or solvent mixtures. Dimethyl formamide, diethyl formamide, acetonitrile, acetone, ethanol, methanol, etc. are commonly used organic solvents. Solvothermal reactions are carried out at temperatures greater than the solvent boiling point. Comparatively higher yield is the major advantage of this method. It provides precise control over the shape distribution, size, and crystallinity of material prepared. Synthesis temperature,

concentration of reactants and pH of the solution should be taken into consideration while using this method. However, removal of solvent molecules from the pores is a complex process and is usually achieved by vacuum drying or washing by solvents such as ethanol or methanol. Pan and his co-workers [11] synthesized three-dimensional zinc-based metal–organic framework $\text{Zn}_2(\text{bpabdc})_2(\text{DMF})_2(\text{H}_2\text{O})_n$ under solvothermal condition and used it as a fluorescent sensor for the detection of cadmium ion and nitrobenzene. Li et al. developed a Cu(II) metal–organic framework $[\text{Cu}(\text{tdc})(\text{H}_2\text{O})]_n \cdot n(\text{DMA})$, under solvothermal condition with CuCl_2 and H_2tdc [12]. Gas adsorption studies showed that the compound can store light hydrocarbons in its desolvated sample. Du et al. synthesized a microporous zinc (II) MOF material, $[\text{H}_2\text{N}(\text{CH}_3)_2] \cdot [\text{Zn}_4(\text{abtc})_2(\text{ad})(\text{H}_2\text{O})] \cdot 4\text{DMF}$ under solvothermal reactions [13]. They used a four-carboxylic acid linker, namely 3,3',5,5'-azobenzene-tetracarboxylic acid and adenine as the organic building blocks to form MOFs. The prepared MOF have shown high selectivity of adsorption of CO_2 over CH_4 and high heat of adsorption of CO_2 . Tzitzios et al. [14] prepared a nanoporous, crystalline metal–organic framework by reacting zinc nitrate and terephthalic acid in dimethyl formamide. The synthesis conditions involved supercritical CO_2 activation and vacuum out gassing procedures. The activated IRMOF-1 showed fully reversible H_2 sorption behavior and gravimetric H_2 uptake. Ji et al. [15] synthesized magnesium-based MOF $[\text{H}_3\text{O}]_2[\text{Mg}(\text{abtc})(\text{DMI})_2]$, under solvothermal condition and applied it as a catalyst in cyano silylation of carbonyl compounds. Porous walls exposed with azo-groups were obtained which facilitated its use as a Lewis base catalyst for the cyano silylation of carbonyl compounds.

Mechanochemical synthesis

Mechanochemical method involves the completion of chemical reaction with the help of mechanical force. Major advantage of mechanochemical synthesis is that the reaction takes place without organic solvents which are carcinogenic, toxic and harmful to environment. In this method, instead of metal salts, metal oxides are usually used as starting materials. Mechanochemical synthesis is simple, economical, and environment friendly. However, only small amount of product is formed in this method. [7, 16, 17]. Chen and his co-workers [18] synthesized indium-based metal organic framework (InOF-1) with excellent water stability mechanochemically and reported as a potential material for CO_2 separation and adsorption. Singh et al. [19] developed rare earth-based metal–organic frameworks by mechanical milling of single and mixed rare earth carbonates with benzene 1,3,5-tricarboxylic acid. These MOFs exhibited magnetic properties below 20 K. Yang et al. performed mechanochemical reaction for preparation of $\text{Cu}_3(\text{BTC})_2$ with emphasis on the effect

of solvent, starting materials, and grinding parameters in mechanochemical synthesis. The results showed that copper acetate produced better yields compared to copper nitrate as starting material. The existence of small amount of solvent increased the crystallinity, BET and Langmuir surface areas of $\text{Cu}_3(\text{BTC})_2$ [20].

Electrochemical synthesis

In electrochemical synthesis, metal ions are provided through anodic dissolution into a reaction mixture containing organic linkers and electrolytes [2]. The major advantage of this method is that the anions associated with metal in salts can be avoided and hence materials produced will be of high purity. Shorter reaction times and milder conditions are required and hence large-scale production of MOFs is possible. Gascon et al. [21] developed several metal–organic frameworks, HKUST-1, ZIF-8, MIL-100(Al), MIL-53(Al), and NH_2 -MIL-53(Al) by anodic dissolution in an electrochemical cell. They studied the effect of reaction variables such as electrolyte, solvent, temperature and voltage–current density on product yield. They also examined textural properties of the prepared MOFs. Li and his coworkers [22] synthesized fluorescent MOF films of $(\text{Zn}_3(\text{btc})_2)$ by applying voltage onto zinc electrodes in 1,3,5-benzenetricarboxylic acid and used for potential applications in identifying nitro explosives with detection limit as low as 0.5 ppm with reusability in successive nitro explosive detection reactions. Campagnol et al. developed MIL-100(Fe) by heating a reaction mixture of 1,3,5-benzenetricarboxylic acid in a 2:1 ethanol:Milli-Q water solvent mixture at high pressure and high temperature in an electrochemical cell [23].

Microwave-assisted synthesis

Microwave-assisted synthesis offers a swift method for the synthesis of MOFs. Nanosized crystals are produced by irradiation of reaction mixture with microwaves. The advantages of this synthesis are high efficiency, less reaction time, phase selectivity, morphology control, particle size reduction, etc. [24–29]. Fan et al. [30] performed microwave-assisted synthesis of zirconium-based metal–organic frameworks. They compared the yield and porosity by changing quantity of modulator, reaction time and temperature. The reaction was completed in 2–2.5 h in microwave which took 24 h for completion in solvothermal method. McKinstry et al. [31] synthesized HKUST-1 using ethanol as the solvent by microwave irradiation. Schlesinger and his coworkers [32] compared different synthetic methods such as solvothermal, microwave-assisted, mechanochemical and ultrasonic method for the preparation of $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$. The microwave-assisted solvothermal synthesis was found to be

better with BET surface area $1499 \text{ m}^2/\text{g}$ and a specific pore volume $0.79 \text{ m}^3/\text{g}$.

Sonochemical synthesis

In this synthesis, a solution of the reaction mixture is subjected to ultrasound (20 kHz–10 MHz) by which molecules undergo chemical change to produce compounds with novel morphologies and unique properties. Within short reaction time, MOFs with small crystal size can be obtained with sonochemical method. Ultrasonic radiation can produce very high temperatures and pressures in the reaction medium. Advantages of this method are that it is generally rapid, economical, reproducible, and environment friendly [29, 33–35]. Armstrong and his coworkers [36] performed the synthesis of the metal organic framework HKUST-1 sonochemically. They studied various parameters such as reactor volume, reaction time, sonication tip size, sonication amplitude, solvent and reactant concentrations. It was found that sonication amplitude and solvent choice affect the particle size distribution, and yield. Morsali et al. developed a three-dimensional cadmium metal–organic framework TMU-7 by ultrasound irradiation [37]. They studied the effects of a variety of factors such as different times of irradiation and various concentrations of initial reagents. Uniform nanoplates were achieved by increasing the time of irradiation. Congo red dye adsorption on these MOFs was efficient due to increase in surface area. Lestari et al. [38] compared electro and sonochemical methods for synthesis of MOF $[\text{Zn}_3(\text{btc})_2]$. Sonochemical method produced higher yield and smaller particle size than the electrochemical method.

Stability of MOFs

Stability is the most crucial factor in the design of MOFs. A MOF must be stable for characterization and for varied application such as sensing, adsorption and catalysis. Stability of MOF means chemical, thermal, hydrothermal and mechanical stabilities. All these stabilities are connected with metal–ligand bond strength. Chemical stability of MOFs can be increased by means of high valence metal ions, such as Cr^{3+} , Fe^{3+} , and Zr^{4+} and by the interactions between soft ligands such as triazolates, imidazolates and tetrazolates. Other nitrogen containing heterocycles can also be used with softer metal ions such as Zn^{2+} , Co^{2+} . The relative stabilities of azolate MOFs are due to strong metal–nitrogen bonds. Divalent metal ions create strong bonds with nitrogen linkers, whereas trivalent metal ions generate strong bonds with oxygen anion-terminated linkers. These MOFs show excellent stability in water [39, 40]. Thermal degradation of MOFs occurs due to node-linker bond breakage, followed by linker combustion. The thermal stability can be increased



by oxy-anion-terminated linkers with higher-valency metal centers. TGA and PXRD can be used to analyze thermal stability. Hydro-thermal stability means stability in the presence of moisture at elevated temperatures. Intermolecular or intramolecular forces, hydrophobic functional groups, per-fluorinated linkers, etc. within MOF structure can increase the hydrothermal stability [41–43]. Mechanical stability of MOFs is connected to their extra-ordinary porosity. Mechanical stability decreases with the increase of porosity. Solvent-filled MOFs are found to be mechanically more stable than MOFs with empty pores [44–48].

MOFs as heterogeneous catalysts

MOFs have been employed in a wide variety of applications such as gas storage, gas separation, catalysis, luminescence, drug delivery, etc. They are found to be highly useful in catalysis due to its porous nature. Heterogeneous catalysis is one of the vital solutions of our developed society, as many chemical processes can be brought about cost effectively using heterogeneous catalyst. MOFs possess fascinating and tailorable properties such as high surface area, permanent porosity and multifunctional ligands. The most important characteristic responsible for their catalytic ability is lack of non-accessible volume. Advantages of MOFs as heterogeneous catalyst are enhanced catalyst reactivity, flexibility, easy tunability, etc. These catalysts possess size, shape, and enantioselectivity. However, due to their low chemical and thermal stability, these are not applicable for reactions that require severe conditions [3, 7, 49, 50]. MOFs were used as a catalyst or catalyst supports for a diversity of organic transformations including Friedel–Crafts reactions [51–55], Knoevenagel condensation [56–60], aldol condensation [61–63], oxidation [64–67], coupling reactions [68–75], cyano silylation [15, 76, 77], carbon dioxide fixation [78, 79], etc (Fig. 1).

Friedel–Crafts reaction

Friedel–Crafts reaction of aromatic compounds is a key process for the preparation of several intermediates in petroleum industry, pharmaceutical, fragrance, flavor, dye and agrochemical industries. They are generally catalyzed by Lewis acids such as AlCl_3 , FeCl_3 , ZnCl_2 and strong mineral acids such as HF. However, catalyst recovery, recycling and product separation are difficult with these catalysts. As these catalysts are moisture sensitive, dry atmosphere is necessary to carry out these reactions. To avoid the drawbacks of homogeneous catalysts, numerous solid acid catalysts have been investigated for the Friedel–Crafts reactions [79–83].

Zhu and co-workers [51] developed a novel urea-containing metal–organic framework and used for Friedel–Crafts

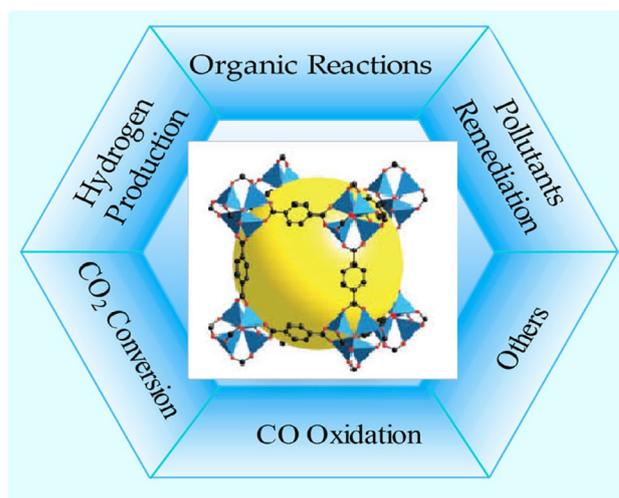


Fig. 1 Versatile applications of MOFs in heterogeneous catalysis

reaction of nitrostyrenes and indoles. They were found to be efficient with excellent product yields at low catalyst loadings. The catalyst demonstrated higher catalytic activity compared to its homogenous urea counterparts. Calleja and coworkers [52] investigated the catalytic properties of Cu-MOF-74 material for the Friedel–Crafts acylation of anisole with acetyl chloride to form methoxyacetophenone. They studied the effect of reaction parameters like the acylating agent, solvent and the reaction temperature. The catalytic activity of Cu-MOF-74 is found to be more active compared to HKUST-1(Cu-MOF), H-ZSM-5 and BETA (aluminum-containing microporous zeolites) and Al-MCM-41 (mesoporous ordered materials). Cu-MOF-74 also showed high stability and reusability. Dhakshinamoorthy et al. compared the catalytic activity of $\text{Cu}_3(\text{btc})_2$, $\text{Fe}(\text{btc})$, $\text{Zr}(\text{bdc})$ and $\text{Zr}(\text{pdc})$ in Friedel–Crafts alkylation reaction of indole with β -nitrostyrene [53]. $\text{Cu}_3(\text{btc})_2$ exhibited higher activity under the optimized reaction conditions without leaching of active sites when performed in different solvents at different temperatures. The catalyst was found to be reusable for four cycles with nominal decrease in its activity and retention of crystalline structure. Phan et al. [54] developed MOF-5 by the reaction between zinc nitrate hexahydrate and 1,4-benzene dicarboxylic acid in *N,N*-diethyl formamide under solvothermal method for Friedel–Crafts benzylation of toluene. *p*-Benzyl toluene was obtained as major product and *o*-benzyl toluene as the minor product under mild conditions. The catalyst was found to be reusable after several catalytic runs. Nguyen et al. [55] synthesized IRMOF-8 under solvothermal condition by the reaction between zinc nitrate tetrahydrate and 2,6-naphthalenedicarboxylic acid in *N,N'* dimethylformamide. They used IRMOF-8 for Friedel–Crafts acylation of toluene with benzoyl chloride to form *p*-benzoyl toluene as the major product and *o*-benzoyl toluene as

by-product. The reaction was carried out at 80 °C for 6 h with 5 mol% IRMOF-8 catalyst with toluene. 50% conversion and 80% selectivity to *p*-benzoyl toluene was observed in the absence of inert atmosphere. IRMOF-8 showed high stability, selectivity and reusability. Other MOFs reported as Friedel–Crafts catalysts is given in Table 1.

Knoevenagel condensation

Gascon et al. [56] developed metal–organic frameworks with non-coordinated amino groups, IRMOF-3 and amino-functionalized MIL-53, for Knoevenagel condensation of ethyl acetoacetate and ethyl cyanoacetate with benzaldehyde. IRMOF-3 displayed 100% selectivity in Knoevenagel condensation. In IRMOF-3 catalysts, aniline-like amino group enhanced the basicity when integrated inside the catalyst structure. The IRMOF-3 catalyst was found to be stable and reusable under reaction conditions.

Hartmann and coworker [57] synthesized three different MOFs, Fe-MIL-101-NH₂, Al-MIL-101-NH₂ and CAU-1. They explored these MOFs in the Knoevenagel condensation of ethyl cyanoacetate and malononitrile with benzaldehyde. The products benzylidene malononitrile and ethyl acyanocinnamate were formed with almost cent percent selectivities with yields of 90–95% after 3 h. The reaction with CAU-1 proceeds slower in contrast to the amino-MIL-101 derivatives. Yang et al. [58] explored the catalytic efficiency of UiO-66-NH₂ in Knoevenagel condensation. They carried out the condensation of benzaldehyde with malononitrile and ethyl cyanoacetate in polar solvents such as DMSO, DMF and ethanol. The UiO-66-NH₂ exhibited higher catalytic activity on comparison with the isostructural amino-free MOF (UiO-66). The catalyst was found to be reusable and stable after several cycles. Xamena et al. [59] considered the catalytic activity of IRMOF-3 and MOF-5 in Knoevenagel condensation of ethyl cyanoacetate and benzaldehyde.

In their work, they made emphasis on the effect of different synthetic procedures of IRMOF-3 and MOF-5 on the Knoevenagel condensation reaction. Callega et al. [60] studied the catalytic activity and stability of amino-based MIL-53(Al) materials in Knoevenagel condensation of malononitrile with benzaldehyde. They modified the amine content using different ratios of 2-amino-benzene-1,4-dicarboxylic acid (NH₂-BDC) and benzene-1,4-dicarboxylic acid as organic ligands during synthesis. The MIL-53(Al) material with equimolar amounts of BDC and NH₂-BDC exhibited more catalytic performance on comparison with other amino-containing MOFs such as UiO-66-NH₂, MIL-101(Al)-NH₂ and IRMOF-3 as well as Na-exchanged beta zeolite.

Aldol condensation

MOFs have been successfully used by different groups in aldol condensation reactions. Koner et al. [61] used an alkaline earth MOF compound, [Ba(pdc)]_n for the aldol reaction of various aromatic aldehydes with cyclohexanone and acetone. They compared catalytic activity in THF, THF/water and solvent-less condition. They found that with increase in the temperature, β-aldol was converted into benzylideneketone. High product formation is observed for electron-withdrawing groups at ortho and para positions of benzaldehyde, whereas lower conversion for electron-donating groups. The catalyst maintained structural integrity and stability after several catalytic reactions. Pathan et al. [62] developed a proficient methodology for the green synthesis of pyrimidine–chalcone using acetophenone and formyl pyrimidines in the presence of [Cu₃(btc)₂(H₂O)₃]. Though Cu₃(btc)₂ was a strong Lewis acid, the catalytic reaction afforded only a negligible conversion on addition of H₂SO₄ to reaction mixture. The catalyst was found to be reusable up to 11th cycle. Kikhtyanin et al. [63] used several MOF like Basosiv M050, Basolite Z1200, (Cu-btc) and (Fe-btc) in aldol condensation

Table 1 MOFs reported as Friedel–Crafts catalysts

| Type of MOF catalyst | Friedel–Crafts reaction | References |
|---|--|----------------------|
| CuMOF (MOF-891) | Synthesis of bis(indolyl)methanes | Nguyen et al. [84] |
| HPW@Zr-BTC | Acylation of anisole with benzoyl chloride | Ullah et al. [85] |
| ZnMOF | Alkylation of indoles with nitroalkenes | Rao et al. [86] |
| Al-based MIL-53 | Alkylation of benzene with ethanol | Rahmani et al. [87] |
| MIL-53(Al) | Acylation of indole with benzoyl chloride | Yan et al. [88] |
| Cu-MOF-74 | Acylation of anisole | Calleja et al. [89] |
| Zr-MOF | Benzoylation of arenes | Doan et al. [90] |
| Urea containing 2D MOF | Friedel–Crafts reaction of indoles and nitrostryenes | Zhu et al. [51] |
| MIL-53(Al)@SiO ₂ @Fe ₃ O ₄ | Acylation of 2-methylindole with benzoyl chloride | Jiang et al. [91] |
| Zn MOF | Alkylation of toluene with benzyl bromide | Farzaneh et al. [92] |
| IRMOF-3-PI-RuCl ₃ | Alkylation of indoles and pyrroles | Khalil et al. [93] |
| Sulfonated Zr- MOF | Acylation of <i>p</i> -xylene with benzoyl chloride | Chung et al. [94] |
| Cu ₄ I ₄ -MOF | Alkylation of indoles with acetals | Zhu et al. [95] |



of acetone and furfural. These reactions were carried out in Parr stirred autoclave under batch conditions at 100 °C. Basosiv M050 and Basolite Z1200 showed insignificant activity, whereas Cu-basolite (Cu-btc) and Fe-basolite (Fe-btc) were active catalysts for the reaction. Acidic centers were attributed as active sites for the aldol condensation over MOFs.

Oxidations

MOFs have been attempted by several groups for oxidation reactions recently. Dhakshinamoorthy et al. [64] studied some metal–organic frameworks for the conversion of silane into silanol using either *t*-butyl hydroperoxide or water as oxidants. $\text{Cu}_3(\text{btc})_2$ exhibited a comparable activity with $\text{Zr}(\text{bdc})$, while the activity of $\text{Fe}(\text{btc})$ is lower than $\text{Cu}_3(\text{btc})_2$ using TBHP as oxidant. On the other hand, $\text{Cu}_3(\text{btc})_2$ showed complete conversion with high selectivity with water as oxidant, but other MOFs like $\text{Fe}(\text{btc})$ and $\text{Zr}(\text{bdc})$ are inactive under identical reaction conditions. Kholdeeva and coworkers [65] prepared Fe- and Cr-containing MOFs, MIL-100 and MIL-101 by solvothermal method and compared the catalytic activities in allylic oxidation of cyclohexene and terpenes with molecular oxygen and oxidation of anthracene with *tert*-butyl hydroperoxide. In the oxidation of alkenes, Fe-containing MOFs produced unsaturated alcohols, whereas Cr-based MOFs gave unsaturated ketones. 100% selectivity was observed for both Cr-MOFs and Fe-MIL-101 with 92–100% anthracene conversion. The stability of MOF enhanced in the order, Fe-MIL-101 < Fe-MIL-100 < Cr-MIL-100, Cr-MIL-101. Kholdeeva et al. [66] also studied the catalytic efficiency of Fe-MIL-101 and Cr-MIL-101 MOFs in the oxidation of α -pinene and cyclohexene at solvent-free conditions. The catalysts performed alkene oxidation at mild conditions and attained allylic oxidation products. Cr-MIL-101 showed selectivity towards α,β -unsaturated ketones whereas Fe-MIL-101 showed selectivity towards 2-cyclohexene-1-ol at 40 °C. Leaching of iron to the solution occurred in case of Fe-MIL-101 at 50–60 °C, leading to cyclohexenyl hydroperoxide. Both catalysts showed better reusability under optimum conditions. Vodyankina et al. [67] investigated the catalytic activity of chromium-based metal–organic frameworks, MIL-101 and MIL-100 in oxidation of propylene glycol using *tert*-butyl hydroperoxide as oxidant. Hydroxyl acetone was obtained as major product, while acetic acid and acetaldehyde were the minor products.

Coupling reactions

Coupling reactions are favorite methods for organic chemists in various organic transformations and fine chemical synthesis. Phan et al. [68] used a decidedly porous metal–organic framework, MOF-199 as heterogeneous

catalyst for Ullmann-type reaction between phenols and aryl iodides forming diaryl ethers. The product yield was 82% after 6 h at 120 °C. MOF-199 catalyst was reusable without noteworthy deterioration in catalytic activity. Chen et al. [69] prepared MOF-253 by hydrothermal reaction of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 2,2'-bipyridine-5,5-dicarboxylic acid, glacial acetic acid, and *N,N*-dimethyl formamide at 120°C for 24 h. Palladium chloride was successfully immobilized on MOF-253, by post-synthetic adaptation. The prepared MOF showed catalytic activity towards Ullmann homo-coupling and Suzuki–Miyaura cross-coupling. MOF-253- PdCl_2 showed higher activity compared to other homogeneous $\text{Pd}(\text{bpy})\text{Cl}_2$ and $\text{PdCl}_2(\text{CH}_3\text{CN})_2$. The superior catalytic performances of metal ions were attributed to charge transfer between metals and adjacent ligands in the catalyst. Nguyen et al. [70] prepared a metal–organic framework $\text{Fe}_3\text{O}(\text{BPDC})_3$ under solvothermal method and used to produce azole derivatives by direct C–N coupling of azoles with ethers by oxidative C–H activation. The leaching studies found that the leached active iron species contributed negligibly to the production of the preferred azole product. The MOF-based catalyst was reused many times without difference in catalytic efficiency. Dhakshinamoorthy et al. [71] explored the catalytic activity of $\text{Cu}_3(\text{btc})_2$ for the dehydrogenative coupling of dimethylphenylsilane with phenol at tolerant circumstances. They observed that $\text{Cu}_3(\text{btc})_2$ exhibited higher stability and activity compared to other MOFs $\text{Fe}(\text{BTC})$, MIL-101(Cr) and UiO-66(Zr) in cross-coupling between dimethyl phenyl silane and phenol. Reusability studies showed that $\text{Cu}_3(\text{btc})_2$ can be reused with minimum deterioration in activity. Brown et al. [72] prepared a series of MOFs, $\text{Zn}_4\text{O}(\text{bdc-NH}_2)_n(\text{bdc})_{(3-n)}$ ($n = 3, 2.4, 1.8, 1.2, 0.9, 0.75, 0.6, 0.3, \text{ and } 0.15$). They modified each compound post synthetically and metalated with Pd, providing the palladium functionalized framework. They exhibited greater activity, selectivity and recyclability in Heck coupling. Corma and co-workers [73] found that copper-containing MOFs were stable, active and reusable solid catalysts for coupling reactions of amines, aldehydes and alkynes forming the consequent propargylamines. Dang et al. [74] prepared Cu-MOF-74 by a solvothermal method and used it for the synthesis of indolizines through aldehyde–amine–alkyne three-component coupling. Cu-MOF-74 showed superior catalytic activity than other Cu-MOFs in three-component coupling reaction. The Cu-MOF catalyst is found to be reusable without significant change in catalytic activity. Zhang et al. [75] synthesized Pd nanoparticles supported on scandium metal–organic frameworks through microwave-assisted impregnation technique. The prepared Pd-Sc btc nano MOFs were better catalysts compared to active carbon supported Pd catalysts in the Suzuki cross-coupling reaction. The catalyst exhibited negligible metal leaching with significant activity in several catalytic runs. Table 2 summarizes other

Table 2 Various MOFs reported for coupling reactions in recent literature

| MOF catalyst used | Coupling reaction | References |
|--|---|------------------------|
| Cu-BDC MOF | Suzuki coupling | Rostamnia et al. [96] |
| UiO-68Se | Aerobic cross-dehydrogenative coupling | Zhang et al. [97] |
| Pd(II)-porphyrinic MOF | Heck coupling | Chen et al. [98] |
| Pd NPs supported on UiO-66-NH ₂ | Suzuki cross-coupling | Kardanpour et al. [99] |
| Pd@MIL-101 | Biginelli and Hantzsch coupling | Rostamnia et al. [100] |
| NPC-Pd MOF | Suzuki–Miyaura coupling | Zhang et al. [101] |
| Transition metal-free MOF | Oxidative coupling of amines | Qiu et al. [102] |
| Cu(4-ba) ₂ (solvent) _n | Chan–Lam coupling, Suzuki–Miyaura coupling, Heck coupling | Wang et al. [103] |
| Cu ²⁺ -M'MOF ZJU-22 | Cross-dehydrogenative coupling | Yang et al. [104] |

MOFs that have been used as catalysts for various coupling reactions.

Cyano silylation

Bharadwaj and co-workers [76] carried out a reaction between an aqueous solution of Zn(NO₃)₂·6H₂O and tetraethylammonium salt of the tripodal ligand *tris*-(4-carboxy-2-phenoxyethyl)amine (ptaH₃) at room temperature. The prepared MOF with coordinatively unsaturated Zn(II) centers were used for Knoevenagel condensation and cyanosilylation reactions successfully. Li et al. [15] synthesized magnesium compound-based 3,3',5,5'-azobenzene-tetracarboxylic acid (H₃O)₂[Mg(abtc)(DMI)₂]_n under solvothermal condition and used as heterogeneous catalyst for the cyanosilylation of carbonyl compounds in solvent-less situation. Significant loss in activity was not observed on reuse. Voort et al. [77] prepared a homochiral vanadium MOF in solvothermal environment. The prepared MOF showed BET surface areas of 574 m² g⁻¹ and exhibited H₂ adsorption capacity and CO₂ uptake. They used it as asymmetric catalyst in solvent-free cyanosilylation. The catalyst was found to be recyclable and reusable for several times. Other catalysts reported for cyanosilylation reactions include Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀]₂ for cyanosilylation of aromatic aldehydes and ketones [105] and Cu₃(BTC)₂ [106].

CO₂ fixation

Babu and co-workers [78] prepared In(III) MOFs with N-donor ligands and carboxylic acids and used as a solid catalyst in CO₂-epoxide cycloaddition reactions. Among the prepared systems, the one-dimensional MOFs containing unsaturated metal centers showed better catalytic efficiency than the two- and three-dimensional MOFs. The same group [79] also prepared a highly porous 3D MOF

[Zn₄O(2,6-NDC)(BTB)_{4/3}] (MOF-205) under microwave method and used its catalytic activity for the CO₂-epoxide coupling reactions to generate five-membered cyclic carbonates at room temperature in solvent-less conditions. They found that the microwave-assisted method is better compared to conventional solvothermal method for catalyst synthesis. The catalyst is found to be reusable up to five cycles. Other MOF catalysts reported in recent literature include MOF-505 [107], triazole containing CuMOF [108] and a CuMOF containing linear tetracarboxylic acid ligand, H₄L, with a pendent amine moiety [109].

Interestingly, MOFs and MOF-based catalysts have been used for a wide variety of organic transformations leading to fine chemical synthesis as well as environmental management recently. A summary of the versatile reactions and catalysts is tabulated in Table 3.

Conclusions

In recent years, MOF materials have become increasingly relevant in chemical industry. The field has been expanding suddenly with the aim of developing new compounds with new structures and fascinating properties. Though different synthetic methods and unlimited number of MOFs with different combinations of linker molecules and metal ions are possible, divalent metal ions with nitrogen linkers and trivalent metal ions with oxygen anion-terminated linkers show comparatively excellent stability. Greener synthesis techniques such as microwave- and sono-assisted methods are gaining momentum. The application of MOFs as heterogeneous catalysts in organic transformations is a developing area of research. They have been widely employed for several transformations such as Friedel–Crafts reactions, condensation reactions, oxidations, coupling reactions, carbon



Table 3 Reactions catalyzed by MOFs and MOF-based catalysts

| MOF catalyst | Type of reaction | References |
|--|---|-----------------------------|
| chiral (salen)Mn MOF | Olefin epoxidation | Cho et al. [110] |
| Cu ₃ (btc) ₂ | rearrangement of α -pinene oxide, cyclization of citronellal | Alaerts et al. [111] |
| [Cu ₂ (BTC) _{4/3} (H ₂ O) ₂] ₆ [H _n XM ₁₂ O ₄₀](C ₄ H ₁₂ N) ₂ | Hydrolysis of esters | Sun et al. [112] |
| [Cd(μ -Cl) ₂] _n MOF | Asymmetric catalysis | Wu et al. [113] |
| Zr-terephthalate MOF | Cross-aldol condensation | Vermoortele et al. [114] |
| Zr metalloporphyrin PCN-222 | Oxidation of pyrogallol | Feng et al. [115] |
| Basolite C 300 | Friedländer reaction | Pérez-Mayoral et al. [116] |
| [Cu ₃ (C ₉ H ₃ O ₆) ₂] ₄ [(CH ₃) ₄ N] ₄ CuPW ₁₁ O ₃₉ H] | Oxidation of thiols | Song et al. [117] |
| Zn ₅ Cl ₄ (BTDD) ₃ | Olefin polymerization | Comito et al. [118] |
| Fe- and Co-functionalized MOFs | Olefin hydrogenation | Manna et al. [119] |
| Cobalt porphyrin MOF | CO ₂ reduction | Lin et al. [120] |
| PCN-222/MOF-545 | Hotoxidation of 2-chloroethyl ethyl sulfide | Liu et al. [121] |
| Porphyrin-based Zr-MOF | Etoxication of dimethyl 4-nitrophenyl phosphate and 2-chloroethyl ethyl sulfide | Liu et al. [122] |
| Lithium-alkoxide doped Zr-MOF | Self-detoxifying filters | López-Maya et al. [123] |
| Ni-S electrocatalyst on MOF scaffolds | Electrochemical hydrogen evolution | Hod et al. [124] |
| InPF-110 | Strecker reaction of ketones | Reinares-Fisac et al. [125] |
| Zr ₆ O ₄ (OH) ₄ (bpydc) ₆ | Arene C–H borylation | Gonzalez et al. [126] |
| Hf-NU-1000 | 1-Hexene polymerization | Klet et al. [127] |
| Hf MOF | Tandem oxidation and functionalization of styrene | Beyzavi et al. [128] |
| Co@NH ₂ -MIL-125(Ti) | H ₂ production | Nasalevich et al. [129] |
| MOOF-based CoP/reduced graphene oxide | Water splitting | Jiao et al. [130] |
| Core-shell Pd@IRMOF-3 nanostructures | Cascade reactions | Zhao et al. [131] |
| MOF-confined Pd@ Co NPs | Hydrolytic dehydrogenation of ammonia borane | Chen et al. [132] |
| Cu ₃ (BTC) ₂ | Aerobic epoxidation of olefins, oxidation of alcohols | Qi et al. [133] |
| Mo-NU-1000 | Cyclohexene epoxidation | Noh et al. [134] |
| Homochiral MOF | Cyanohydrin synthesis | Mo et al. [135] |
| Zr-MOF with Me ₂ Mg | Hydroboration and hydroamination | Manna et al. [136] |
| Co nanoparticle-embedded carbon@Co ₉ S ₈ | Oxygen reduction | Hu et al. [137] |
| N-doped CNTs derived from MOF | Oxygen electrocatalyst | Xia et al. [138] |
| Ni-Zr-NU-1000 | Gas-phase hydrogenation | Li et al. [139] |
| Fe-porphyrin-MOF | Electrochemical reduction of CO ₂ | Hod et al. [140] |
| Pd nanocubes@ZIF-8 | Hydrogenation of olefins | Yang et al. [141] |
| Hf-NU-1000 | CO ₂ fixation, enantioselective epoxide activation | Beyzavi et al. [142] |
| MIL-101-Cr-SO ₃ H-Al(III) | Fixed-bed reactions | Li et al. [143] |
| Mn-Zr-MOF | Photocatalytic CO ₂ reduction | Fei et al. [144] |
| BINAP-based MOFs | Pauson–Khand reaction between 1,6-enynes and carbon monoxide | Sawano et al. [145] |

dioxide fixation, etc. to name a few. Recently, the thrust has shifted to shape selective catalysis owing to their regular structure and porosity.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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